KANSAS STATE UNIVERSITY

MANHATTAN, KANSAS

SEMI-ANNUAL STATUS REPORT

Infrared Laboratory Studies of

Synthetic Planetary Atmospheres

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This report covers work for the period

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It was prepared by

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I. ABSTRACT OF RESEARCH TO DATE

The general program represents an extension and generalization of an earlier program dealing chiefly with telluric gases. The basic instrumentation includes three Perkin-Elmer Model 112 spectrometers equipped with prisms to cover the range between the visible and 40 microns, one Perkin-Elmer Model 421 grating instrument for the 2- to 18-micron region, and a Perkin-Elmer Model 301 far-infrared spectrograph for the region 12 to 330 microns; this basic instrumentation was supplied by Kansas State University.

The initial stages of the research have been involved with a test of Burch's Law of multiplicative transmittance of mixed absorbing gases for broadening of the absorption lines by H_2 and He, which are constituents of the atmospheres of the major planets. Other early work has been concerned with the broadening of lines in the CO fundamental by a variety of gases; the results indicate that the effects of H_2 and He are such that corrections must be made to observed band shapes if one is to arrive at valid estimates of the temperatures of planetary atmospheres by spectroscopic techniques. Other work has been done on the absorptance of atmospheric gases at reduced temperatures and on the more exact determination of the bandstrengths for absorbing atmospheric gases.

Cumulative List of Publications*

1. "Further Studies of Overlapping Absorption Bands," Tubbs, Hathaway, and Williams, J. Opt. Soc. Amer. 57, 570 (1967) P.
2. "Foreign-Gas Broadening of Absorption Lines in the CO Fundamental," Draegert, Chai, and Williams, J. Opt. Soc. Amer. 57, 570 (1967) P.
3. "Broadening of Absorption Lines in the CO Fundamental," Chai, Draegert, Williams, Bull. Am. Phys. Soc. 12, 542 (1967). P.
4. "Further Studies of Overlapping Absorption Bands," Tubbs, Hathaway, and Williams, App. Opt. (Presented for publication)

* P denotes a paper presented at a scientific meeting.

II. PROGRESS DURING THIS REPORT PERIOD.

A. Absorption by Overlapping Bands.

The appended brief report of this work has been presented for publication as a letter in Applied Optics. No further work on the subject is at present contemplated.

B. Line-Broadening Coefficients.

Appended are abstracts of papers presented at the spring meetings of the Optical Society of America and the American Physical Society.

C. Band Strength Measurements.

Work has been done on a re-determination of band strengths S but has been interrupted by the failure of certain components when subjected to high pressures; reconstruction is in progress. No reports are ready for publication.

D. Absorption of Gases at Reduced Temperatures.

A great deal of effort has gone into this work but no results are yet ready for publication. The results should be of use in interpreting the details of planetary spectra.

III. PERSONNEL

Dr. Dudley Williams, Regents' Professor of Physics:

Chief Investigator (WOC)

Dr. Charles E. Hathaway, Assistant Professor of Physics:

Senior Associate (WOC)

Dr. Basil Curnutte, Professor of Physics:

Senior Associate (WOC)

Gary M. Hoover, B. A., M. A.: Research Assistant (Half-Time)

An-Ti Chai, B. S., M. S.: Research Assistant (Half-Time)

Lloyd Tubbs, B. S.: NASA Fellow.

IV. PLANS FOR THE NEXT REPORT PERIOD

A. Studies of self-broadening and foreign-gas broadening of the rotation-vibration bands will be continued.

B. Work on band strengths will be continued.

C. Studies of atmospheric gases at reduced temperatures will be continued.

Submitted 7 June 1967

Signed Dudley Williams
Dudley Williams

Appended Reports:

"Foreign-Gas Broadening of Absorption Lines in the CO Fundamental," Draegert _et al_

"Broadening of Lines in the CO Fundamental," Chai _et al_

"Further Studies of Overlapping Bands," Tubbs _et al_

"Further Studies of Overlapping Absorption Bands," Tubbs _et al_

Foreign-Gas Broadening of Absorption Lines in the CO Fundamental*

(Title of paper, in upper and lower case)

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The relative foreign-gas broadening coefficient F is defined by the relation $F = p_N/p_b$, where p_b is the partial pressure of gas b required to give the same total absorptance as that produced by nitrogen at partial pressure p_N when the same absorber thickness w is used. F-values of several foreigh gases applicable to the entire CO fundamental have been re-determined at low resolution by single-beam techniques. The present values of F are as follows: H_2, 1.17; D_2, 0.95; He, 0.80; A = 0.80; CH_4, 1.11; and NH_3, 1.59. These values are believed to be accurate to ±10 percent. Present F-values for H_2 and He are not in agreement with earlier values determined by double-beam techniques.[1] Values of $F(\nu)$ appropriate to various portions of the CO band have also been determined under conditions of high as well as low resolution. For H_2, D_2, and He, the values of $F(\nu)$ in the band wings are approximately 50 percent greater than $F(\nu)$-values near the band center. Values of $F(\nu)$ for CO_2 and N_2O have been determined in spectral regions where absorptance of these gases does not overlap the CO fundamental.

*Supported in part by Air Force Cambridge Research Laboratories and by NASA.

1. Singleton, Burch, and Williams, Appl. Opt. 1, 359 (1962).

Broadening of Absorption Lines in the CO Fundamental.* An-Ti Chai (introduced by Dudley Williams), David A. Draegert, and Dudley Williams, Kansas State University--The integrated spectral absorptance $\int A(\nu)d\nu$ of an absorption line of Lorentz shape is related to the half-width of the line. The half-width can be expressed in terms of an equivalent total pressure $P_e = Bp_a + p_{ref}$, where p_a and p_{ref} are the partial pressures of the absorbing gas and a non-absorbing reference gas, respectively. The parameter B is the ratio of the "line-broadening ability" of the absorbing gas to that of the reference gas. In the present study, values of B have been determined for individual rotational lines in the CO fundamental when various reference gases are employed. With N_2 as the reference gas, B is nearly constant for all frequencies. With H_2, D_2, and He as reference gases, B is considerably larger near the band center than in the wings; the reverse variation of B is obtained when A, Kr, and Xe are used as reference gases. Comparisons between the effects of various molecules on CO molecules in different rotational states will be noted. Various interaction mechanisms between colliding molecules will be discussed.

*Work supported in part by Air Force Cambridge Research Laboratories and by NASA.

Further Studies of Overlapping Absorption Bands*
(Title of paper, in upper and lower case)

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Previous studies have indicated that the spectral transmittance of a mixture of atmospheric gases is equal to the product of the transmittances of the constituents measured separately provided the same absorber thicknesses are used and provided the total pressure of all samples is made the same by the addition of nitrogen. For mixtures of CO_2 and water vapor[1] and for CO-N_2O and CO-CH_4 mixtures[2], the multiplicative relation has been found to hold even in the extreme case in which the total pressure is equal to the sum of the partial pressures of the absorbing gases. However, it was suggested[2] that for non-absorbing gases other than nitrogen it might be necessary to specify a total equivalent pressure to take account of the different line-broadening abilities of the non-absorbing gases. In the present study of overlapping CO and N_2O bands, He and H_2 were used as line broadeners. The simple multiplicative law applies in close approximation when the partial pressure of the non-absorbing gas is large compared with the partial pressures of the absorbing gases but must be modified when the partial pressures of the absorbing and non-absorbing gases are comparable.

*Supported in part by Air Force Cambridge Research Laboratories.

1. Burch, Howard, and Williams, Jour. Opt. Soc. Amer. 46, 452 (1956).

2. Hoover, Hathaway, and Williams, Appl. Opt. (In Press).

Further Studies of Overlapping Absorption Bands *

Lloyd D. Tubbs, C. E. Hathaway
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It is well known that the spectral transmittance of a mixture of two gases of given absorber thicknesses does not necessarily equal the product of the spectral transmittances of the same gases measured separately [1,2]; i.e. $T_{12}(\nu) \neq T_1(\nu) \cdot T_2(\nu)$. However, it was found by Burch et al.[3] that under certain conditions the measured transmittances do obey the simple multiplicative relationship

$$T_{12}(\nu) = T_1(\nu) \cdot T_2(\nu). \quad \text{(Burch's Law)} \tag{1}$$

Burch's study indicated that (1) holds provided (a) the absorber thicknesses of the individual absorbers are the same for the samples being compared; (b) the spectral slit width is sufficiently broad to include several absorption lines; and (c) the total pressure P is made the same in all samples by the addition of nitrogen. Burch showed that relation (1) is valid for overlapping bands of CO_2 and H_2O vapor; the line spacings and intensities of H_2O - vapor bands are essentially "random" and the line spacings and intensities of the overlapping CO_2 bands are "regular."

More recent work[4] has demonstrated that Burch's Law (1) could be applied successfully to overlapping bands of CO and N_2O in the 2200 cm^{-1} region and to overlapping bands of N_2O and CH_4 in the 1300 cm^{-1} region even when relatively narrow slits were employed. In these cases the region of overlap includes regularly spaced lines for which the line spacings are incommensurate.

Although the requirement that the total pressure be constant appeared sufficient for measurements of transmission through the earth's atmosphere, Hoover et al.[4] suggested this requirement might not be sufficient if a non-absorbing gas other than N_2 is used to provide equal total pressures. If the line-broadening effects produced by collisions between the broadening and absorbing molecules differ greatly from the effects produced by collisions between absorbing molecules, it was also suggested that it might be necessary to introduce an effective pressure

$$P_e = \sum_a B_a p_a + \sum_b F_b p_b \qquad (2)$$

where p_a is the partial pressure of each absorbing gas; p_b is the partial pressure of each line-broadening, non-absorbing gas; B_a is the self-broadening coefficient for each absorbing gas relative to N_2; and F_b is the foreign-gas broadening coefficient relative to N_2 appropriate to each non-absorbing gas present[5].

The present study of the overlapping bands of CO and N_2O in the 2200 cm^{-1} region was undertaken to ascertain the possible need for use of an effective pressure (2). Hydrogen and helium, which are abundant in the atmospheres of the outer planets, were chosen as the non-absorbing, broadening gases. Their F-values are appreciably different from unity; the average F-values of hydrogen and helium for the fundamental band of CO are 1.17 and 0.80, respectively[6].

A Perkin—Elmer 112 spectrometer equipped with a CaF_2 prism was used. With the mechanical slit width held constant, the spectral slit width varied from 10 to 15 cm^{-1} over the spectral region of interest. A 30 cm stainless-steel absorption cell was employed.

The upper panel of Fig. 1 shows the spectral transmittance of a CO-N_2O mixture with p_{CO} = 60 Torr and p_{N_2O} = 6 Torr. Curves A show results obtained when He was added to give a total pressure of one-quarter of an atmosphere. The top curve in set A gives the product of the individual spectral-transmittance measurements. The lower curve in set A is the measured transmittance of the CO-N_2O mixture. The top curve in set B is the transmittance of the CO-N_2O mixture with H_2 as the broadening gas; the lower curve is the product of the individual transmittances. The difference between the transmittance computed from Burch's Law and the measured transmittance with He as the broadening gas is at most +2% and occurs near the center of the N_2O band. The corresponding difference in transmittance is -3% near the center of the N_2O band with H_2 as the broadening gas. The agreement of Burch's Law with the measured transmittance of a mixture becomes closer as the partial pressure of the broadening gas is further increased.

The lower panel of Fig. 1 shows the spectral transmittance of overlapping CO-N_2O bands for partial pressures of 40 Torr of CO and 4 Torr of N_2O. Curves C were obtained with He as the broadening gas; Curves D give results obtained with H_2 as the broadening gas. All measurements were made at a total pressure of 44 Torr. The measured transmittance of the CO-N_2O mixture with no broadening gas present is shown by the solid curves. The dot-dash curves show the spectral transmittance computed from (1). The difference between the computed transmittance and the measured transmittance for the mixture is +3% near the center of the N_2O band for helium broadening and is -3% near the center of the N_2O band for hydrogen broadening. Even in these extreme cases, there is thus fair agreement between the transmittance computed from Burch's Law and the measured transmittance.

Closer agreement between computed transmittance and the measured transmittance of the CO-N_2O mixture can be obtained by using an effective pressure

$$p_E = p_{CO} + p_{N_2O} + F_b p_b \tag{3}$$

with F_b as a single adjustable parameter. "Best fit" curves are shown by the dashed curves in the lower panel. These curves were obtained with an F-value of 0.82 for He and with an F-value of 1.4 for hydrogen. When expression (3) is used as a criterion for equal equivalent pressure, the greatest difference between computed and measured transmittance is +1% near the center of the N_2O band.

The present results indicate that one may safely employ Burch's Law without modification in studies of planetary atmospheres since the error introduced by using the simple product relationship (1) is considerably less than other uncertainties involved in transmissions measurements.

REFERENCES AND FOOTNOTES

1. K. Angstrom, Phys. Rev. 1, 597 (1892).
2. E. von Bahr, Ann Physik 29, 780 (1909); 33, 585 (1910).
3. D. E. Burch, J. N. Howard, and D. Williams, J. Opt. Soc. Amer. 46, 452 (1956).
4. G. M. Hoover, C. E. Hathaway, and D. Williams, App. Op. 6, 481 (1967).
5. D. E. Burch, E. B. Singleton, and D. Williams, App. Op. 1, 359 (1962).
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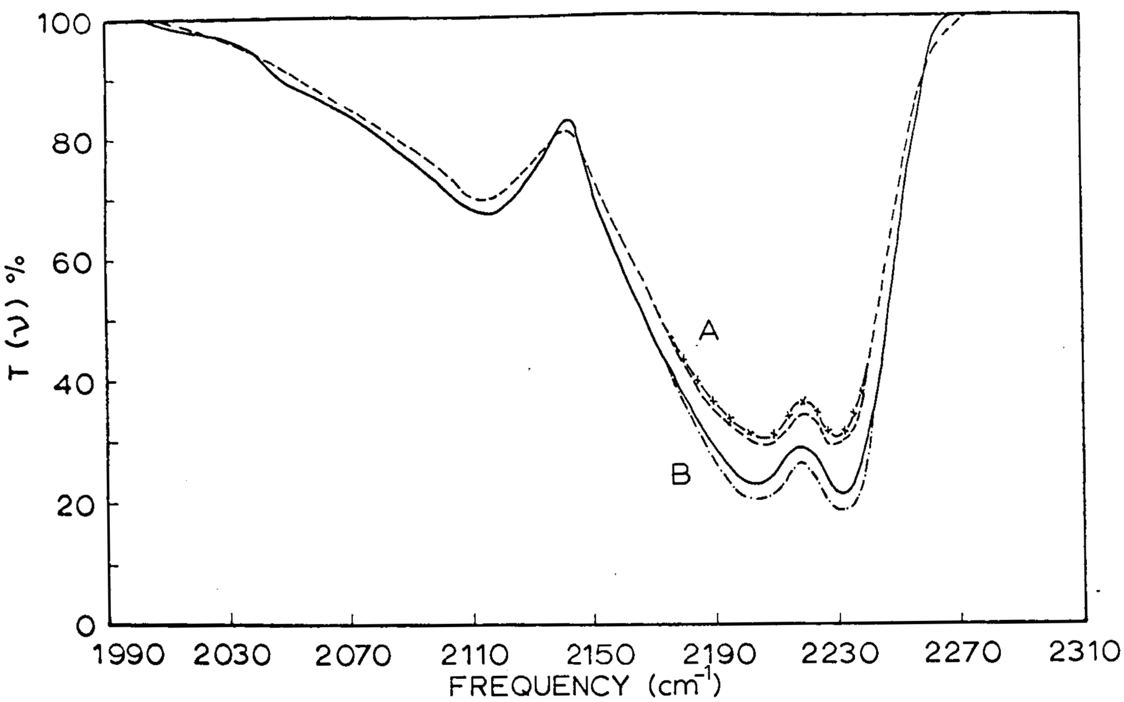
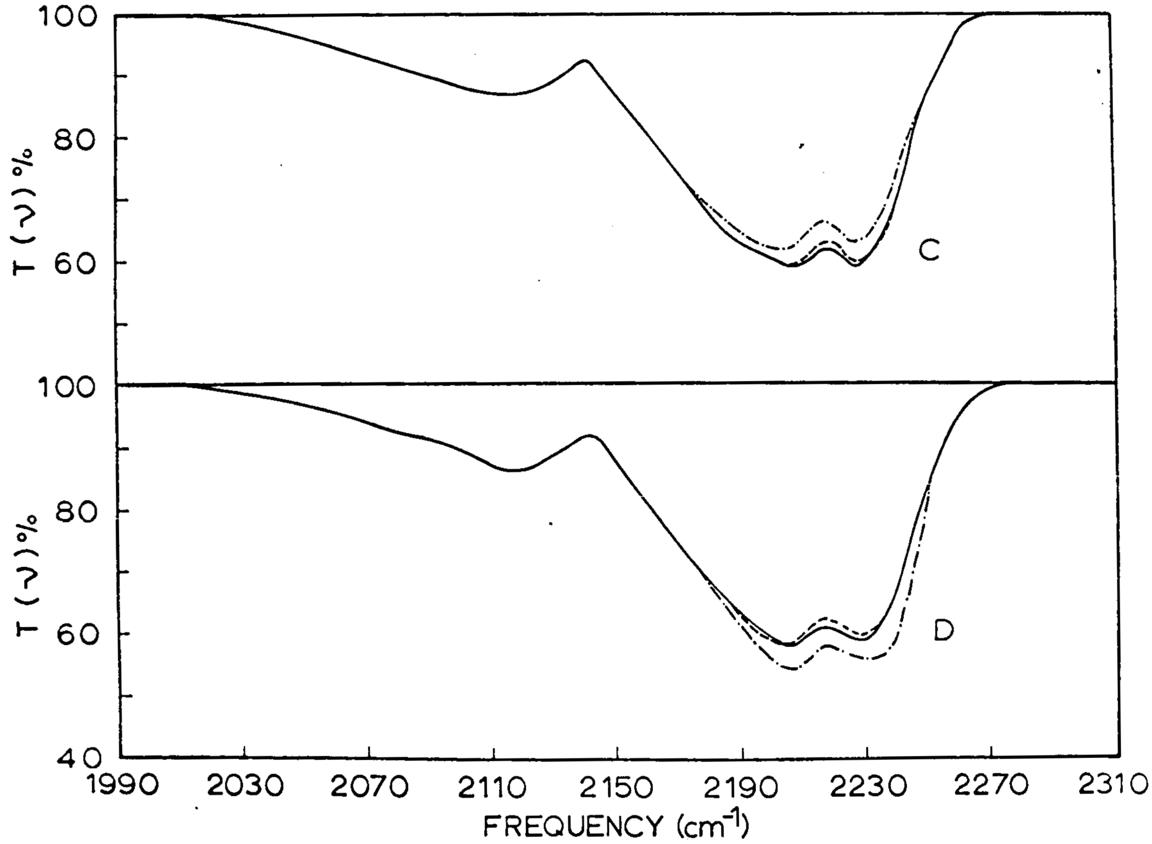
Legend for Figure

Fig. 1 Low-resolution study of overlapping bands of CO and N_2O in the 2200 cm^{-1} region. The upper panel shows the bands at total pressure of one-quarter atmosphere with He (A) and H_2 (B) as the broadening gas. The measured transmittance is shown by the dashed line (A) and the solid line (B) and the product $T(CO) \cdot T(N_2O)$ is shown by the cross-dash (A) and dot-dash lines (B).

The lower panel shows the overlapping bands at a total pressure of 44 Torr with no broadening gas present in the mixture. The calculated spectral transmittance is shown by the dot-dash curves for He (C) and H_2 (D) as the broadening gas and the measured transmittance is given by the solid curves. The "best fit" curves are shown by the dashed curves.



100
80
60
40
20
0
T (ν) %
A
B
1990 2030 2070 2110 2150 2190 2230 2270 2310
FREQUENCY (cm⁻¹)



100
80
60
T (ν) %
C
100
80
60
40
T (ν)%
D
1990 2030 2070 2110 2150 2190 2230 2270 2310
FREQUENCY (cm⁻¹)